

INFLUENCE OF Sm-Cr DOPING ON STRUCTURAL AND MAGNETIC PROPERTIES OF M-TYPE STRONTIUM HEXAFERRITE

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Strontium hexaferrite nanoparticles substituted with samarium and chromium having nominal composition $\text{SrFe}_{12-2x}\text{Sm}_x\text{Cr}_x\text{O}_{19}$ ($x=0.0, 0.4, 0.8$) have been synthesized by WOWS (With Out Water and Surfactants) sol-gel method. X-ray diffraction (XRD) studies showed that higher doping concentration results in the formation of impurity phases. Due to higher ionic radius of doped rare earth ion, Sm, lattice parameter “c” has increased. Doping of Sm-Cr caused the increase in grain growth confirmed from scanning electron microscope (SEM) images. Coercivity almost doubles for $x=0.4$ and afterward decreases due to the formation of impurity phase. Similar trend is observed for saturation magnetization and retentivity.

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1. Introduction

Ferrites are very important class of magnetic materials from application point of view and are extensively used as permanent magnets in market because of their low price, high magnetic performance, and have attracted attention over years [1]. The very high specific resistance and remarkable flexibility in the magnetic properties makes the ferrite ideal choice material for telecommunication, operational frequency of electronic devices and microwave applications [2]. Ferrites can be divided into three categories namely spinel, hexagonal and garnets according to their crystal lattice structure [3]. Ferrites with the chemical formula $\text{AFe}_{12}\text{O}_{19}$, where A is most often Ba or Sr, are those ferrites which have magnetoplumbite structure commonly called as hexagonal structure. All the M-type hexaferrite compounds crystallize in a magnetoplumbite structure with close-packed O layers, where one O is replaced by one A (Ba or Sr) in every fifth layer and where Fe occupies five different interstitial sites: three octahedral sites ($12k, 2a,$ and $4f_2$), one tetrahedral ($4f_1$) site and one bi-pyramidal site ($2b$) [4]. Magnetoplumbite ferrites are suitable for electromagnetic interference suppression and radar absorbing materials due to their strong magnetic losses at giga hertz frequency [1].

Novel properties due to reduced dimensions are responsible for attraction of magnetic nanoparticles [5]. It has been illustrated that some magnetic properties depend on particle size and particle size distribution [6]. Strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) belongs to the family of M-type hexaferrites having a hexagonal magnetoplumbite structure with space group $P63/mmc$ [7].

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Strontium hexaferrite nanoparticles have been the focus of great research activities because of its relatively large magnetization, high coercivity and chemical stability [8].

High coercivity originates from the highly anisotropic crystal structure of magnetoplumbite hexaferrite, which strongly depends on particle size and shape [9]. The hexagonal structure of hexaferrites allows having extremely high intrinsic magnetocrystalline anisotropy. This gives them a unique combination of dielectric and magnetic properties at high frequencies and is suitable for microwave frequency region [10, 11] due to their uni-axial magnetic anisotropy [12–13].

Researchers are now interested to improve the saturation magnetization and electrical resistivity, reduce the grain size and to make the materials suitable for applications in magnetic recording media and microwave devices. For this purpose, various transition metal cations are doped at iron as well as at strontium site with partial success [14–16]. Furthermore, the intrinsic magnetic properties of Sr-hexaferrite are found to be affected by the partial substitution for Sr or Fe sites, or both. For example, a significant improvement has been obtained in $\text{SrFe}_{12}\text{O}_{19}$ hexaferrites by the substitution of Sr^{2+} site by La^{3+} [17], Nd^{3+} [18], Sm^{3+} [19], Fe^{3+} ions by magnetic ions such as Cr^{3+} [20] and Co^{2+} [21] ions and non-magnetic ions such as Al^{3+} [22], Zn^{3+} [23], Ga^{3+} [24] and Cd^{3+} [25] and replacement of $\text{Sr}^{2+}/\text{Fe}^{3+}$ together with Pr–Zn [26], La–Cu [27], and La–Zn [28]. The electrical and magnetic [29] properties of M-type hexa-ferrites can be tailored by using different dopants on these interstitial sites.

The preparation method and the type of cation substitution were found to have significant influence on the magnetic properties of strontium hexaferrite. Accordingly, several methods had been used to prepare hexaferrite particles including sol–gel method [30], gel-combustion method [31], hydrothermal process [32], ammonium nitrate melt technique [33], ceramic route [34], co-precipitation method [35, 36], and polymerizable complex method [37]. Ball milling method had been recently employed for the preparation of strontium ferrite powders [38, 39].

In the present study, we have reported a detailed investigation on structural, magnetic, electrical and dielectric properties of Sm and Cr co-substituted strontium hexaferrite $\text{SrFe}_{12-2x}\text{Cr}_x\text{Sm}_x\text{O}_{19}$, for ($x = 0.0, 0.4, 0.8$) nanoparticles. The aim of the present work is to improve the properties of strontium hexa-ferrites and making the material useful for high frequency applications.

2. Synthesis

M-type $\text{SrFe}_{12-x}\text{Sm}_x\text{Cr}_x\text{O}_{19}$ with ($x=0.0, 0.4, 0.8$) were prepared by sol gel method. The chemicals used in the synthesis of samples were $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The stoichiometric amounts of precursors in the nitrate form are dissolved in calculated amount of ethylene glycol one by one at temperature of 100°C with stirrer rate 200 revolutions per second. To obtain gel, solution is heat treated at 250°C with stirrer rate 250 revolutions per minute. The solution was then converted in to gel like material. The gel was burned at higher temperature 300°C . The dried material was grinded and converted in to powder form. Some powder is converted in to pallet. The as prepared powder and pellets were heat treated at 950°C for 90 minutes.

3. Results and discussion

3.1 X-ray diffraction

In order to identify the phase and crystallinity of the prepared samples, X-ray diffraction (XRD) patterns are obtained and are shown in Fig. 1. The obtained patterns are indexed with standard ICDD-01-079-1411 and ICDD-01-079-1412. All the samples exhibit the main characteristic peaks of magnetoplumbite structure. The peak appearing in sample $x=0.8$ at position 33.18 is representing the presence of extra phase of $\alpha\text{-Fe}_2\text{O}_3$.

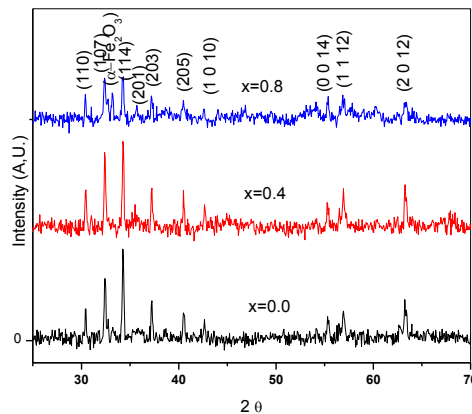


Fig 1. Indexed XRD patterns of $SrFe_{12-2x}Cr_xSm_xO_{19}$ ($x=0.0, 0.4, 0.8$).

Lattice parameters (a , c) and crystallite size (D) have been extracted from XRD patterns and listed in Table 1.

Crystallite size and lattice constant can be obtained from XRD data by using following formulae.

Lattice constants can be measured by using [50]

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

hkl are miller indices

Size of crystal is measured by using

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (2)$$

where ' λ ' is wavelength, β is FWHM (Full width at half maximum) and ' θ ' is Bragg angle

Volume of unit cell is calculated by using

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (3)$$

It is observed that the value of parameter ' a ' remains almost constant but c increases with increasing doping amount of Cr-Sm. Lattice parameter c increases due to difference of ionic radii of samarium and iron.

Table 1. Calculated lattice parameters (a , c) and cell volume from indexed XRD patterns of $SrFe_{12-2x}Cr_xSm_xO_{19}$ ($x=0.0, 0.4, 0.8$)

Sample	X=0.0	X=0.4	X=0.8
a (Å)	5.868	5.875	5.87
c (Å)	22.984	23.034	23.06
V_{cell} (Å ³)	685	688	689

3.2 Scanning electron microscopy (SEM)

Fig. 2 illustrates the SEM micrographs of the M-type hexaferrite $SrCr_xSm_xFe_{12-2x}O_{19}$ for sample $x=0.0$, $x=0.4$ and $x=0.8$ sintered at 950 °C for 1.5 h. It is observed from the SEM micrographs that the grain particles of the sintered magnets are hexagonal platelet-like shape. The particle size has increased and started to agglomerate when doping concentration has increased.

The voids present on the surface that confirms the porous nature of strontium hexaferrite. The particle size is in the range of 80-300 nm.

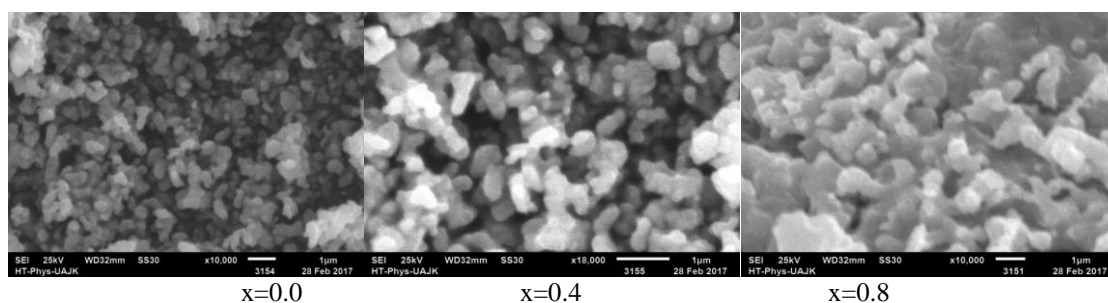


Fig 2. SEM images of $SrFe_{12-2x}Cr_xSm_xO_{19}$ ($x=0.0, 0.4, 0.8$).

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of annealed and undoped strontium hexaferrite powder given in Fig. 3 shows four significant absorption peaks at 1596 cm^{-1} , 1556 cm^{-1} , 487 cm^{-1} and 416 cm^{-1} . The first two peaks are due to C=C stretching bonds and last two peaks are related to the Fe–O stretching vibrational band in octahedral and tetrahedral sites [40, 41].

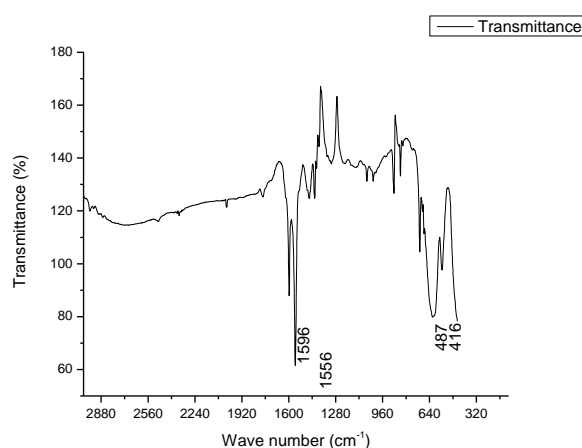


Fig 3. FTIR spectra of $SrCr_x-Sm_xFe_{12-2x}O_{19}$ for $x=0.0$.

3.4 Magnetic properties

Fig. 4 shows the hysteresis loop for $SrFe_{12-2x}Sm_xCr_xO_{19}$ (where $x=0.0, 0.4, 0.8$). The values of saturation magnetization (M_s), remanence magnetization (M_r) and coercivity (H_c) are calculated by using these hysteresis loops. It is clear from the figure that the values of both M_s and H_c increase with Sm–Cr content upto $x \leq 0.4$ and then decrease with further increase in dopant concentration. The value of saturation magnetization and coercivity has increased for doping $x=0.4$ and then decreased for $x=0.8$. Sm with magnetic moment of $1.5\mu_B$ occupies the interstitial site with spin down [40]. As a result, net magnetic moment increases and hence saturation magnetization increases. It may also due to increase in particle size. For higher doping concentration, extra phase of $\alpha\text{-Fe}_2\text{O}_3$ appears due to which net magnetization decreases. The coercive force obtained for $x=0.4$ given in Table 2 is much bigger than that of $SrFe_{12}O_{19}$ particles reported in literature [42].

Table 2. Values of particle size, coercivity, saturation magnetization and retentivity obtained from hysteresis loops of $SrFe_{12-2x}Cr_xSm_xO_{19}$ ($x=0.0, 0.4, 0.8$).

Sample	X=0.0	X=0.4	X=0.8
Particle size (nm)	200	280	300
Coercivity (H_c) G	3561.7	6530.2	3842.0
Magnetization (M_s) emu	0.2862	0.3267	0.2425
Retentivity (M_r) emu	0.1783	0.2038	0.1533

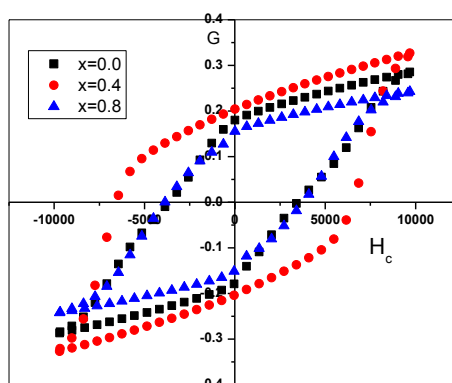


Fig. 4. Hysteresis loop of $SrFe_{12-2x}Cr_xSm_xO_{19}$ ($x=0.0, 0.4, 0.8$).

4. Conclusions

The Sm–Cr substituted strontium hexaferrites are synthesized by the sol–gel method. The XRD data shows that material has single magnetoplumbite phase. Higher concentration of doping constant resulted in the formation of extra phase of $\alpha\text{-Fe}_2\text{O}_3$. SEM images confirmed the homogenous formations of the particles.

The particle size has increased with the increase in doping content and their distribution is narrow. The substitution of Sm–Cr leads to increase in saturation magnetization due to increase in particle size and net magnetic moment. Coercivity for the sample $x=0.4$ is maximum and make the sample suitable for high frequency applications.

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